
Broken Symmetry Approach to Calculation of Exchange Coupling Constants for Homobinuclear and Heterobinuclear Transition Metal Complexes

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ABSTRACT: The application of broken symmetry density functional calculations to homobinuclear and heterobinuclear transition metal complexes produces good estimates of the exchange coupling constants as compared to experimental data. The accuracy of different hybrid density functional theory methods was tested. A discussion is presented of the different methodological approaches that apply when a broken symmetry wave function is used with either Hartree–Fock or density functional calculations. © 1999 John Wiley & Sons, Inc. J Comput Chem 20: 1391–1400, 1999

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Introduction

Progress in the experimental study of binuclear transition metal complexes and their magnetic properties has been outstanding in the last decades.¹ From the theoretical point of view, the magnetic behavior of such compounds has been qualitatively studied by several authors by analyzing the trends of the magnetic coupling constant by means of the Hay–Thibeault–Hoffmann model.² However, such an approach is restricted to the antiferromagnetic component of the coupling constant and has limited predictive ability for the magnetic properties of new compounds. An alternative strategy consists of the direct *ab initio* evaluation of the exchange coupling constant J defined in the spin Hamiltonian $H = -J\vec{S}_1 \cdot \vec{S}_2$, where \vec{S}_1 and \vec{S}_2 are the local spin operators for each of the paramagnetic centers. For instance, for a system with two unpaired electrons, the coupling constant corresponds to

$$J = E_S - E_T, \quad (1)$$

where E_S and E_T are the energies of the singlet and triplet states, respectively, and in principle can be accurately calculated at a high level of theory.

It must be noted that to obtain the coupling constant one has to calculate energy differences that are usually smaller than 100 cm^{-1} ($\sim 0.3 \text{ kcal/mol}$) from total energies 7 or 8 orders of magnitude larger. Given the degree of accuracy needed for estimations, the most theoretically sound method is the use of a multideterminantal approach as reported by several authors.^{3–11} However, such methodology is computationally demanding and usually the use of simplified model structures is required to reduce the number of atoms in the calculation. An alternative is provided by the broken symmetry (BS) approach that was proposed by Noodleman et al.^{3,12–16} This approach consists of performing unrestricted [either Hartree–Fock (UHF) or density functional theory (DFT)] calculations for low spin open-shell molecular systems in which the α and β densities are allowed to localize on different atomic centers, which is referred to as BS calculations. This strategy was originally developed for HF or HF–Slater methods, but it was recently used in combination with “pure” density functional methods. A clear advantage of the use of DFT over the post-HF

methods resides in its ability to handle large systems, as shown by us recently for hydroxo, alkoxo,^{17,18} oxo,¹⁹ oxalato,²⁰ and oxamidato²¹ Cu(II) binuclear complexes, as well as for azido-bridged Cu(II), Ni(II), and Mn(II) complexes.²²

The present article has two distinct goals. First, we wish to test the performance of different hybrid density functional methods for the evaluation of the magnetic exchange coupling constants by comparing them with the literature values obtained by fitting magnetic susceptibility data to a spin Hamiltonian, especially for the case of heterobinuclear transition metal complexes. At the same time we try to clarify the applicability of the BS approach using different single-determinant methods.

Computational Details

All the calculations presented here were performed using the Gaussian 94 program.²³ Local density contributions were estimated using the Slater exchange functional²⁴ and the Vosko, Wilk, and Nusair²⁵ (VWN) expression for the correlation functional. Generalized gradient corrections were introduced using Becke’s expression²⁶ for the exchange part (B), combined with that proposed by Lee, Yang, and Parr²⁷ (LYP) for the correlation part. We employed four different hybrid approaches that mix the exact exchange with density functionals: the method recently proposed by Becke²⁸ with only one parameter ($a_0 = 0.28$), using the LYP correlation functional (B1LYP); the two-parameter method (B2LYP)²⁹ in which $E_{xc} = c_0 E_x^{\text{HF}} + c_1 E_{xc}^{\text{DFT}}$, with values of 0.332 and 0.575 for the c_0 and c_1 parameters, respectively, as proposed by Becke, and applied by Nishino et al. for the calculation of exchange coupling constants³⁰; the widely used B3LYP method³¹; and the half and half method (HHLYP) as originally introduced by Becke, including only half of the correlation energy.²⁹

For the $\text{H}\cdots\text{He}\cdots\text{H}$ system, the 6-311G(d,p) basis set was employed for the UHF, CASSCF(4,4), and DFT calculations. The atomic spin densities for the evaluation of the overlap integral [see Appendix, eq. (A.10)] were obtained through natural bond orbital (NBO) and Mulliken population analysis with the 6-31++G(d,p) basis set to allow comparison with previous results from other authors. For the metal complex calculations, the basis sets proposed by Schaefer et al. were employed that were triple ζ quality for the transition metal

atoms³² and double ζ quality for the other atoms.³³ We previously showed that this combination provides very similar results to those of a triple ζ basis set for all the atoms with a considerable savings of computer time.¹⁷

The calculation of the magnetic exchange coupling constants for the transition metal complexes was carried out using the experimental geometries of the different compounds. No geometry optimization was attempted because very small variations in the geometry such as those induced by the packing forces in the crystal can lead to large changes in the calculated coupling constant, making comparison with the experimental value meaningless.

BS Wave Functions and Evaluation of Coupling Constant

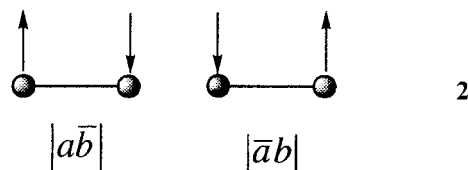
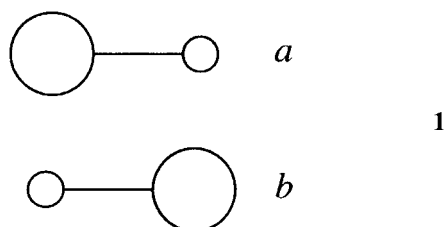
For a system with two unpaired electrons in two nonorthogonal orbitals a and b localized on two different atoms (schematically depicted in 1), it is possible to construct the $M_s = 1$ component of the high spin state as a Slater determinant,

$$\Phi(S = 1, M_s = 1) = \frac{|ab|}{(2 - 2\langle a|b \rangle^2)^{1/2}}, \quad (2)$$

whose energy can be calculated easily. On the other hand, one can describe the lowest singlet state by using BS wave functions. From localized molecular orbitals, a BS wave function (schematically depicted in 2) was defined by Noodleman and Case¹⁴ as a single-determinant expression of the singlet state.

$$\sigma_{BS}^1 = |a\bar{b}|/\sqrt{2}. \quad (3)$$

Obviously, an alternative BS solution (2) can be defined as $\sigma_{BS}^2 = |\bar{a}b|/\sqrt{2}$. The BS wave functions are not eigenfunctions of the total spin operator, but an adequate singlet function can be obtained



as a linear combination of the two BS determinants:

$$\Phi(S = 0) = \frac{\sigma_{BS}^1 - \sigma_{BS}^2}{\sqrt{2 - 2\langle \sigma_{BS}^1 | \sigma_{BS}^2 \rangle}}. \quad (4)$$

A wave function for the $M_s = 0$ component of the triplet state could also be constructed from the two BS solutions,

$$\Phi(S = 1, M_s = 0) = \frac{\sigma_{BS}^1 + \sigma_{BS}^2}{\sqrt{2 + 2\langle \sigma_{BS}^1 | \sigma_{BS}^2 \rangle}}. \quad (5)$$

However, the calculation of the energy for the $M_s = 1$ component [eq. (2)] is straightforward, and there is no need for such an approach.

Calculating the energy for the wave function in eq. (4) and subtracting from the energy of the triplet yields the following expression³⁴ for the singlet–triplet gap:

$$J = \frac{2(E_{BS} - E_T)}{1 - \langle \sigma_{BS}^1 | \sigma_{BS}^2 \rangle}. \quad (6)$$

To estimate J using eq. (6), one must calculate the overlap integral $\langle \sigma_{BS}^1 | \sigma_{BS}^2 \rangle$. If spin polarization of the inner shells is neglected, that integral can be approximately calculated from the overlap integral between the two singly occupied molecular orbitals (SOMOs) a and b as proposed by Caballol et al.³⁴:

$$J = \frac{2(E_{BS} - E_T)}{1 + \langle a|b \rangle^2}. \quad (7)$$

As an alternative to directly calculating the overlap integral in eq. (7) one can estimate it from the calculated spin densities at the metal atoms in the triplet (T) and BS states (see Appendix), resulting in the following expression, which applies only to symmetric binuclear complexes with one unpaired

electron per paramagnetic center:

$$J = \frac{2(E_{\text{BS}} - E_{\text{T}})}{1 + \rho_{\text{T}}^2 - \rho_{\text{BS}}^2}. \quad (8)$$

For the general case of a system with more than one unpaired electron per metal center and a value of the total spin $S = S_1 + S_2$ in the highest spin (HS) state, an expression for J as a function of the BS and HS state energies can be obtained assuming only that the SOMOs are orthogonal,¹⁴ resulting in the relationship originally proposed by Noodleman et al., who referred to this approximation as the *weak bonding* regime.

$$J = \frac{2(E_{\text{BS}} - E_{\text{HS}})}{S^2}. \quad (9)$$

For the particular case of a binuclear system with one unpaired electron per center, such an expression is equivalent to assuming that the spin orbitals a and b are fully localized [i.e., $\langle a|b \rangle^2 \approx 0$ in eq. (7)], resulting in

$$J = 2(E_{\text{BS}} - E_{\text{T}}). \quad (10)$$

Finally, the use of the spin-projected method proposed by Nishino et al.³⁰ allows one to estimate the value of J through the following expression:

$$J = \frac{2(E_{\text{BS}} - E_{\text{HS}})}{\langle S^2 \rangle_{\text{HS}} - \langle S^2 \rangle_{\text{BS}}}. \quad (11)$$

Evaluation of Coupling Constant from DFT Calculations

When using BS calculations to obtain quantitative estimates of the exchange coupling constant, a crucial problem is to decide which wave function to use to estimate the energy of the singlet state. Within the density functional framework, Baerends et al. indicated that the single-determinant wave function includes all the electron correlation contributions to the energy, even the nondynamic correlation.³⁵ In DFT calculations the energy of the singlet state can be approximated in principle using that of the single-determinant BS state σ_{BS}^1 , which was confirmed by the good results obtained by Perdew et al.³⁶ for the atomization energy of H_2 with such approximation to the energy of the singlet. These authors indicated that such a BS state describes the electron density and the on-top electron pair density with remarkable accuracy,

even if it gives an unrealistic distribution of the spin density, and propose that the BS single-determinant wave function is the correct solution for the Kohn–Sham equations. Miehlich et al.³⁷ presented the findings of a recent attempt to combine density functionals with multideterminant wave functions that avoid a double counting of the correlation energy. Following the same line of thought, Wittbrodt and Schlegel³⁸ discussed the influence of spin projection on the DFT study of potential energy surfaces. By comparing them with full configuration interaction (CI) results for dissociation energy curves, these authors showed that the spin projection improves the UHF and UMP2 results whereas the best results from DFT methods are obtained with the energy values of the broken symmetry state without spin projection.

It is clear that for BS HF calculations the use of eq. (4) should provide a better estimate of the singlet state energy.^{39–41} Hence, eq. (6) [or one of its approximate solutions, eqs. (7)–(11)] should be used in combination with UHF calculations. In contrast, for DFT calculations we adopt single-determinant wave functions [eqs. (2), (3)] for which the DFT is well defined,^{36,37,42} taking into account the precedents discussed in the previous paragraph. In this context, the singlet–triplet gap can be expressed by

$$J = E_{\text{BS}} - E_{\text{T}}. \quad (12)$$

Such an expression corresponds with the non-spin-projected energy. A more general expression that also applies to systems with more than one unpaired electron per center with local spins S_1 and S_2 (where $S_2 \leq S_1$) is

$$J = \frac{(E_{\text{BS}} - E_{\text{HS}})}{2S_1S_2 + S_2}, \quad (13)$$

which can be expressed in the following way for those compounds with the same spin on the two centers ($S_1 = S_2$; $S = S_1 + S_2$):

$$J = \frac{2(E_{\text{BS}} - E_{\text{HS}})}{S(S + 1)}. \quad (14)$$

In the following we discuss the results of DFT and UHF calculations on a simple hypothetical $\text{H}\cdots\text{He}\cdots\text{H}$ system to compare the values of J calculated through the two different approaches with those obtained from full CI calculations. Then we report on similar calculations for binuclear transition metal complexes and compare the results with experimental data.

H···He···H System

The simplest system one can think of in which two unpaired electrons couple through a superexchange pathway is that formed by two hydrogen atoms bridged by an He atom. Although no experimental information exists for such system, its small size makes it possible to perform full CI calculations and it has become a standard benchmark.^{34, 43, 44} For that reason we chose this system to analyze the performance of the DFT methods in calculating the coupling constant through the single-determinant approach discussed in the previous section.

Table I presents the values of the singlet–triplet gap for the hypothetical H···He···H molecule obtained by applying eq. (13) to the results of DFT calculations with different functionals. The table also shows the same gap calculated at the UHF and CASSCF(4,4) levels, as well as the full CI results reported by other authors,^{34, 44} for comparison. Results for other post-HF methods and for pure DFT methods can be found in a recent work by Bencini et al.⁴⁴ Our results clearly indicate that the use of eq. (13) for hybrid density functional methods gives good approximations to the full CI values at different distances, the best results being those obtained from B3LYP calculations, that practically match the accuracy of the CASSCF(4,4) method. The error of the B3LYP results relative to

the full CI values is smaller than 15%, although it must be stressed that the absolute error for those J values that are small enough to be relevant for the magnetic behavior at room and lower temperatures (i.e., for H—He ≥ 1.625 Å) is at most 13 cm⁻¹. Also, the pure DFT method BLYP yields quite good results, although we will see below that its performance for more complex systems becomes poorer. Results reported by other authors⁴⁴ using pure functionals give poorer agreement with the full CI values than the results obtained here with hybrid methods.

As expected, the calculation of the singlet–triplet gap from the UHF energies through eq. (13) yields too small values of J that are due to the use of a non-spin-projected single-determinant wave function. However, if the spin-projected expressions [eqs. (8) or (11)] are used to estimate the gap from the UHF calculations, the results are comparable to those obtained from full CI calculations (Table I). These findings are in good agreement with the results reported by Illas and Martin⁴⁵ for magnetic coupling constants in cluster models of KNiF₃, K₂NiF₄, and La₂CuO₄. By using eq. (8) combined with a method that employs an equal mixture of DFT and exact exchange without any correlation functional contribution, these authors obtained good agreement between the calculated coupling constants and the values deduced from the experimental critical temperatures using the mean field theory.

TABLE I.
Exchange Coupling Constants J (cm⁻¹) for
H···He···H System at Different H–He Distances
Deduced from Calculated Energies of Triplet and
Broken-Symmetry States.

Method	d (Å)		
	1.250	1.625	2.000
BLYP	–5391	–621	–69
HHLYP	–2855	–330	–36
B1LYP	–3577	–420	–47
B2LYP	–3865	–483	–57
B3LYP	–4367	–513	–57
UHF [eq. (13)]	–1947	–210	–20
UHF [eq. (11)]	–3498	–414	–40
UHF [eq. (8)]	–3694	–417	–40
CASSCF(4, 4)	–4304	–487	–49
Full CI ³⁴	–4860	–544	–50

All values were obtained through eq. (13), except where otherwise specified. The spin densities used in eq. (8) were obtained from an NBO population analysis.

Application to Binuclear Complexes

Focusing now on the more complex systems in which we are interested (homobinuclear and heterobinuclear transition metal complexes), we wish to study the applicability of single-determinant UHF calculations combined with the different approximations to estimate the value of J [eqs. (8)–(11), (13)] and compare them with the results of different hybrid functionals using DFT calculations together with eq. (13). For this purpose we selected an antiferromagnetic oxalato-bridged Ni(II) complex⁴⁶ and a ferromagnetic hydroxobridged Cu(II) complex.⁴⁷ Two heterobinuclear complexes were also included to extend the scope of these calculations, which so far had been applied only to homobinuclear complexes. The selected compounds are a phenoxo-bridged copper-vanadyl complex,⁴⁸ and an oxamido-bridged Mn(II)–Cu(II) compound.⁴⁹

The results of BS-UHF calculations for these compounds were used to estimate the values of J by applying eqs. (10), (11), and (13) (Table II). In general, it can be seen that eqs. (9) and (13) give practically the same results, which are in qualitative agreement with the experimental data in both the sign and the magnitude of the exchange interaction. Especially remarkable is the excellent agreement found for the Cu(II) complex for which eq. (8) also provides a good estimate ($J = 112 \text{ cm}^{-1}$) due to the strong localization of the wave function at the metal centers. For the other complexes with more than one unpaired electron per metal atom, eq. (8) cannot be applied and a better agreement with the experimental data is found with hybrid DFT methods, as will be shown below.

In a previous article¹⁷ we compared the ability of several widely used density functionals to calculate the magnetic exchange coupling constant for hydroxo- and alkoxo-bridged binuclear Cu(II) complexes. The hybrid B3LYP method was found to give better results than either the GGA or local density approximation approaches. Recently, Becke proposed different expressions for the mixing of the exact HF-type exchange and the exchange cor-

relation terms in density functional methods. As stated in the introduction, one of the goals of this study was to test the performance of different hybrid functionals on binuclear complexes covering a wide range of magnetic behaviors. In Table III we present the exchange coupling constants of four complexes obtained with DFT-based methods in combination with the BS approach [eq. (13)]. Among the five functionals tested here, important differences can be appreciated between the BLYP results and those obtained with hybrid methods. The coupling constants calculated with hybrid methods seem to be dependent on the amount of exact exchange included. Thus, we obtained similar values for all of them except the HHLYP method in which the contribution of the exact exchange is larger. The best agreement with the experimental values was obtained using the B3LYP functional, even if similar accuracy is reached with the B1LYP and B2LYP functionals. For all four complexes, the non-projected results of the B3LYP method (Table III) yielded better agreement with the experimental data than the spin-projected UHF calculations [eq. (11), see Table II].

The HF method is usually considered to overestimate the relative stability of the triplet state in

TABLE II.
Calculated Exchange Coupling Constants (cm^{-1}) for Complete Structures of Binuclear Complexes Using UHF Method and Spin-Projected [Eqs. (9) or (11)] or Non-Spin-Projected [Eq. (13)] Expressions and Expectation Values of Total Square Spin Operators Used for Eq. (11).

Compound	$\langle S^2 \rangle_{\text{HS}}$	$\langle S^2 \rangle_{\text{BS}}$	Eq. (13)	Eq. (9)	Eq. (11)	Expt
$[\text{Cu}_2(\mu\text{-OH})_2(\text{bipym})_2](\text{NO}_3)_2$	2.0073	1.0182	+56	+112	+113	+114 (ref. 47)
$[\text{Ni}_2(\mu\text{-ox})(\text{Medpt})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	6.0093	2.0098	-3	-4	-4	-22 (ref. 46)
$[\text{CuVO}(\text{fsa})_2\text{en}] \cdot \text{CH}_3\text{OH}$	2.1539	1.1557	+19	+38	+38	+118 (ref. 48)
$[\text{CuMn}(\text{obze})(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$	12.0067	7.0067	-4	NA	-5	-34 (ref. 49)

bipym, 2,2'-bipyrimidine- N,N' ; (fsa)₂en, N,N' -(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane; Medpt, 3,3'-diamino- N -methyl-dipropylamine; obze, oxamido- N -benzoato- N' -ethanoato; ox, oxalate. NA, eq. (9) does not apply to compounds with different numbers of unpaired electrons at two metal atoms.

TABLE III.
Exchange Coupling Constants (cm^{-1}) for Binuclear Complexes Calculated from DFT Energies of HS and BS States through Eq. (13).

Compound	BLYP	HHLYP	B1LYP	B2LYP	B3LYP	Expt
$[\text{Cu}_2(\mu\text{-OH})_2(\text{bipym})_2](\text{NO}_3)_2$	+221	+72	+105	+86	+113	+114
$[\text{Ni}_2(\mu\text{-ox})(\text{Medpt})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	-108	-7	-17	-16	-27	-22
$[\text{CuVO}(\text{fsa})_2\text{en}] \cdot \text{CH}_3\text{OH}$	^a	+37	+48	+46	+52	+118
$[\text{CuMn}(\text{obze})(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$	-180	-13	-22	-27	-42	-34

Experimental data also provided for comparison. See Table II for references and abbreviations.

^a The BS solution obtained with this functional presents an unrealistic distribution of the spin population.

contrast with the local DFT methods that show the opposite behavior.⁵⁰ The present calculations offer the opportunity to analyze how the relative stability of the high and low spin states changes when varying the contribution of the HF-type exchange. Among the presently tested methods, the exact exchange contribution increases in the order BLYP < B3LYP < B1LYP < B2LYP < HHLYP < UHF. The representation of the logarithm of $|J|$ calculated with the different methods (Fig. 1) clearly shows that the high spin/low spin splitting decreases with the HF-type contribution, regardless of the high or low spin nature of the ground state. The computational results for the copper-vanadium complex follow a similar trend but were not included in the figure because of the poorer agreement with the experimental value and the lack of an adequate BLYP solution.

Although there is limited data to establish firm conclusions, comparison of the calculated values of J with the experimental data for the binuclear complexes or with the full CI results for the $\text{H}\cdots\text{He}\cdots\text{H}$ system is highly interesting. We wish to remark that these results allow us to rationalize the problems faced in the past with the calculation

of exchange coupling constants and provide an explanation for the good results that are being obtained with hybrid functionals. The pure functionals may overestimate the energy gap, whereas the UHF calculations may underestimate it. Even if the spin projection formula is applied to the UHF results, increasing the calculated value of $|J|$ by a factor of $2/S^2$ [eqs. (9) and (12)] is not enough to reproduce the experimental values well, given the logarithmic scale of Figure 1. It is also interesting to note that the effect of the relative weights of HF and DFT contributions is very different from one system to another, which probably explains why in some cases the calculations give better results than in others. The experimental or full CI results appear to be well reproduced by those functionals that incorporate around 25% of the exact exchange, namely the B3LYP and B1LYP ones. These results are also consistent with the expression proposed by Perdew et al.,⁵¹ including one-quarter of the exact exchange, which also gave excellent results for the atomization energies of a variety of small molecules. Some recently developed hybrid functionals also incorporate the exact exchange with a weight of 0.25 and should thus be regarded as interesting alternatives for the calculation of exchange coupling constants in the light of our computational results. These include B1LYP and *m*PW1PW,^{52,53} both of which well reproduce experimental bond distances, bond angles, and atomization energies for diatomic and small polyatomic molecules, or the parameter-free functional PBE0.⁵⁴

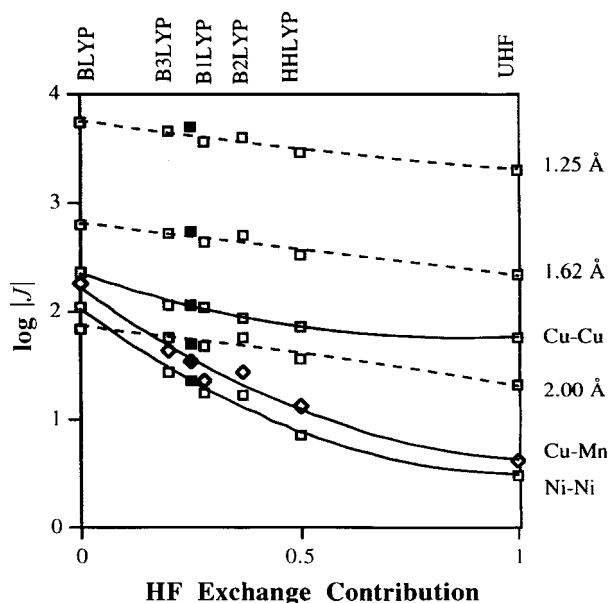


FIGURE 1. Variation of the absolute value of J (logarithmic scale) as a function of the exact exchange contribution of UHF and different DFT methods calculated for (—) transition metal binuclear complexes and (---) the $\text{H}\cdots\text{He}\cdots\text{H}$ system at different distances. The experimental data for the complexes and the previously reported full CI results³⁴ for $\text{H}\cdots\text{He}\cdots\text{H}$ are represented by filled symbols.

Conclusions

When the exchange coupling constant is evaluated by applying the BS approach to the results of UHF calculations, a two-determinant wave function must be used to estimate the energy of the singlet state. The exchange coupling constant can be adequately calculated through eqs. (8) or (10). In symmetric binuclear compounds with one unpaired electron per center, a proposed formula allows us to calculate the singlet–triplet gap with good approximation from the calculated atomic spin densities. The proposed methodology gives good results compared to the full CI calculations for the benchmark $\text{H}\cdots\text{He}\cdots\text{H}$ system and reasonable estimates compared to experimental values for four test binuclear transition metal complexes.

Good estimates of the coupling constant can be obtained with density functional methods by directly using a single-determinant BS wave function to estimate the energy of the singlet state [eq. (13)]. Of the different functionals tested, the widely used B3LYP is the one that yielded the best results for the $\text{H}\cdots\text{He}\cdots\text{H}$ system as compared to full CI calculations. The application of the same methodology to test binuclear complexes gave better agreement with the experimental data than with spin-projected UHF calculations. An alternative approach for DFT calculations would imply the application of spin projection [eq. (6)] to BS solutions using hybrid functionals with a larger weight of the HF component as proposed by Illas and Martin.⁴⁵ The present approach does not apply to molecules with strictly degenerate SOMOs, such as O_2 , because its two orthogonal π^* orbitals cannot be represented as localized orbitals a and b (1). For this case, DFT calculations with spin projection seem to give good results.⁵⁵ Among other authors that chose to use density functional calculations together with spin projection, interesting results were reported for cyano-bridged complexes in a recent article by Nishino and coworkers.⁵⁶

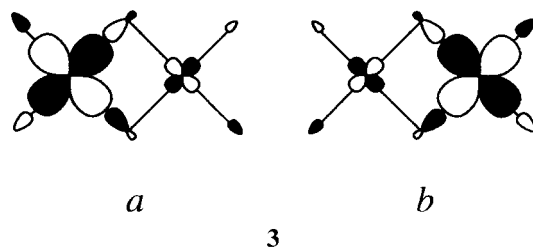
Appendix

The overlap integral between the SOMOs, $\langle a|b \rangle$, needed in eq. (7) can in principle be calculated, but calculation is not straightforward with most of the standard computational packages. Hence, an interesting approach consists of approximating such an integral³⁴ from the calculated spin population at the metal atoms in the BS state. For homobinuclear complexes the expression reported is

$$\langle a|b \rangle^2 \approx 1 - \rho_{\text{BS}}^2. \quad (\text{A.1})$$

However, such an approximation provides results comparable to those obtained by direct calculation of the overlap integral only for systems with highly localized SOMOs and may give imaginary values of the overlap integral if $\rho_{\text{BS}} > 1$. To avoid this problem we propose a slightly different approach.

For homobinuclear complexes, the localized molecular orbitals schematically depicted in **1** can be best described as in **3**. Such molecular orbitals are built up from atomic orbitals at the two metal centers (χ_1 , χ_2) and linear combinations of the



ligands' orbitals, φ_L and φ'_L :

$$a = \alpha\chi_1 + \beta\chi_2 + \gamma\varphi_L, \quad (\text{A.2})$$

$$b = \beta\chi_1 + \alpha\chi_2 + \gamma\varphi'_L, \quad (\text{A.3})$$

where $\alpha \gg \beta, \gamma$ because of localization. For the case of a symmetric complex, $\langle \chi_1|\varphi_L \rangle = \langle \chi_2|\varphi'_L \rangle \gg \langle \chi_1|\varphi'_L \rangle = \langle \chi_2|\varphi_L \rangle$. The overlap integral between the molecular orbitals can be written as

$$\begin{aligned} \langle a|b \rangle &= 2\alpha\beta + \gamma^2\langle \varphi_L|\varphi'_L \rangle + (\alpha^2 + \beta^2)\langle \chi_1|\chi_2 \rangle \\ &\quad + 2\gamma[\alpha\langle \chi_2|\varphi_L \rangle + \beta\langle \chi_1|\varphi_L \rangle]. \end{aligned} \quad (\text{A.4})$$

Assuming important localization of the orbitals at the metal centers, we can neglect the terms with coefficients β^2 , γ^2 , and $\beta\gamma$, as well as the integral $\langle \chi_2|\varphi_L \rangle$. By considering that one is dealing with bridged complexes in which the interaction is due to a superexchange mechanism, the direct overlap between the metal atomic orbitals can also be neglected, $\langle \chi_1|\chi_2 \rangle \approx 0$. With such approximations, eq. (A.4) becomes

$$\langle a|b \rangle \approx 2\alpha\beta. \quad (\text{A.5})$$

The same result is obtained for the simpler $\text{H}\cdots\text{He}\cdots\text{H}$ system by considering that the a and b orbitals are mostly localized on the hydrogen atoms, which was actually found in the calculations. Assuming that the molecular orbitals a and b are identical in the triplet and BS states, the spin population at the metal atoms in the triplet and BS states can be expressed as follows by applying a Mulliken population analysis scheme:

$$\begin{aligned} \rho_T &= \alpha^2 + \beta^2 + 2\alpha\beta\langle \chi_1|\chi_2 \rangle \\ &\quad + \gamma(\alpha\langle \chi_1|\varphi_L \rangle + \beta\langle \chi_1|\varphi'_L \rangle), \end{aligned} \quad (\text{A.6})$$

$$\rho_{\text{BS}} = \alpha^2 - \beta^2 + \gamma(\alpha\langle \chi_1|\varphi_L \rangle - \beta\langle \chi_1|\varphi'_L \rangle). \quad (\text{A.7})$$

These expressions can be simplified by adopting the same approximations as above together with

$\gamma\alpha\langle\chi_1|_L\rangle \ll \alpha^2 + \beta^2$, resulting in

$$\rho_T \approx \alpha^2 + \beta^2, \quad (\text{A.8})$$

$$\rho_S \approx \alpha^2 - \beta^2. \quad (\text{A.9})$$

Finally, combining eqs. (A.5), (A.7), and (A.9), we obtain a simple expression for the overlap integral as a function of the atomic spin densities at the metal atoms in the triplet and BS states:

$$\langle a|b\rangle^2 \approx \rho_T^2 - \rho_{BS}^2. \quad (\text{A.10})$$

Notice that the applicability of such an expression as deduced here is limited to symmetric binuclear complexes with one unpaired electron per paramagnetic center. Also, such an expression would result in imaginary values of the overlap integral whenever the absolute value of the calculated spin population at the metal atom is smaller in the triplet than in the BS state. It is expected to work better for systems with highly localized unpaired electrons. Although the present expression was deduced assuming one unpaired electron per metal atom in a homobinuclear complex, its extension to systems with a larger number of unpaired electrons can be envisioned. This kind of equation can be useful for solid-state calculations where the HF method is widely used to study magnetic systems, and it would improve the accuracy of the estimates of energy differences between the spin states in such systems.^{57–59}

As a check of the applicability of eq. (A.10), Table A.I shows the overlap integral for the $\text{H}\cdots\text{He}\cdots\text{H}$ system, which was obtained from the atomic spin densities calculated through either an NBO⁶⁰ or a Mulliken population analysis. The NBO results are in excellent agreement with those

corresponding to the direct estimation of the overlap integral,³⁴ whereas the Mulliken population analysis yields somewhat poorer results. We recall, however, that eqs. (A.1) and (A.10) cannot be applied in those cases in which the BS spin population is larger than that of the triplet state, because an imaginary value of the overlap integral would result.

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TABLE A.I. Spin Densities and Overlap Integral $\langle a|b\rangle$ between Two SOMOs in $\text{H}\cdots\text{He}\cdots\text{H}$ at Different H–He Distances Calculated According to Eqs. (A.1) and (A.10) (Applying Mulliken or NBO Population Analyses) Compared to Exact Value.

Method	d (Å)		
	1.250	1.625	2.000
ρ_T (Mulliken)	1.0628	1.0202	1.0068
ρ_{BS} (Mulliken)	1.0240	1.0159	1.0062
ρ_T (NBO)	0.9627	0.9878	0.9966
ρ_{BS} (NBO)	0.9354	0.9854	0.9963
$\langle a b\rangle$ [eq. (A.1), NBO]	0.3536	0.1705	0.0860
$\langle a b\rangle$ [eq. (A.10), Mulliken]	0.2855	0.0936	0.0347
$\langle a b\rangle$ [eq. (A.10), NBO]	0.2279	0.0701	0.0232
$\langle a b\rangle$ (exact ³⁴)	0.2347	0.0761	0.0247

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